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(54) A CATHETER OR TUBE HAVING A TIP WHICH IS HIGH IN OPACITY  
TO X-RAYS

(71) We, WARNE SURGICAL PRODUCTS LIMITED, a British Company of Trevor House, 100 Brompton Road, London, SW3 1EL, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the making of a catheter or tube having a tip which is high in opacity to X-rays.

At present the tips of catheters and tubes produced from extruded plastic tubing have been rendered high in opacity to X-rays by extruding a continuous or disconnected line of a substance high in opacity to X-rays simultaneously as the tube is extruded.

20 An alternative method has been to heat-weld a radio-opaque washer or insert onto that end of the tube or catheter which passes into the patient, hereafter referred to as the patient end.

25 The previously proposed methods, however, involve somewhat complicated equipment and it is a general object of this invention to provide a simple method of applying the highly X-ray opaque material.

30 Therefore according to the invention there is provided a method of making a catheter or tube useful for medical or surgical purposes having at the patient end (as herein defined) a coating of a finely-divided substance high in opacity to X-rays, in which, to the patient end is applied a paste comprising the finely-divided substance which is high in opacity to X-rays and which has a particle size of not greater than one micron, dispersed in a solution of a synthetic polymer dissolved in at least one organic solvent which is evaporatable and which will soften the synthetic plastics material of which the patient end is made and allowing the solvent to evaporate to give the coating.

45 Catheters and tubes made in this way have a strongly bonded highly X-ray opaque coating at the patient end because the sol-

vent has softened the material of the patient end and so formed an excellent body between that material and the synthetic polymer in which the highly X-ray opaque substance is dispersed.

50 The organic solvent or solvents in which the polymer is dissolved, is preferably cyclohexanone, methyl ethyl ketone, tetrahydrofuran or a combination of any of these solvents. The solvent chosen is capable of evaporating off once a catheter tip has been coated with the paste. Also the solvent is capable of softening at least the surface portion of a plastics catheter tip immersed in the paste so giving, after drying, an excellent bond between the material of the catheter and the dried polymer which acts as a binder for the finely-divided, highly X-ray opaque material.

55 The paste may be applied very readily to catheters or tubes made from synthetic polymeric materials by first immersing the part of the tube to be rendered high in opacity to X-rays i.e. the patient end, into the paste to the required depth by hand or mechanical means. The immersed portion is then withdrawn slowly to prevent runs or uneven deposits and is air or vacuum dried to remove the solvent. By this method the paste forms an integral part of the tube or catheter and is permanently bonded thereon.

60 Alternatively the paste can be applied to the tip by use of transfer printing, brushing or spraying.

65 One method of producing the paste comprises dissolving chips of the synthetic polymer in the organic solvent, or a combination of solvents, and agitating to produce an even smooth, viscous saturated solution. A substance having a high opacity to X-rays is ground or milled to give a particle size of not greater than one micron. This highly X-ray opaque powder is then added to the polymer solution, which is stirred gently until all the powder is completely wetted. The resultant paste is filtered through a 250 wire mesh to remove lumps, and any air bubbles

are removed by applying a vacuum or agitating.

The weight of the highly X-ray opaque substance in the paste is preferably about equal to that of the polymer.

The synthetic polymer used in the paste is preferably either polyvinyl chloride or polyurethane.

The highly X-ray opaque substance is preferably bismuth, precipitated barium sulphate or tungsten.

The invention will now be illustrated by the following Examples of pastes which are useful in applying to the patient end of a catheter or tube by the method according to the invention.

#### Example 1

100 grams of P.V.C. chip is dissolved in an organic solvent e.g. cyclohexanone (Sextone), methyl ethyl ketone or a combination of such solvents, and agitated to give a viscous saturated solution.

100 grams of a highly X-ray opaque substance e.g. bismuth, precipitated barium sulphate or tungsten is ground or milled to a particle size of not greater than 1 micron. The highly X-ray opaque powder is then added to the P.V.C. solution and thoroughly dispersed in it to give a paste.

This paste can then be applied to P.V.C. tubing.

#### Example 2

A dipping paste is prepared by the same method as set out in Example 1, except that the P.V.C. chip is replaced by polyurethane chip. The polyurethane chip can only be dissolved in tetrahydrofuran.

The paste made from polyurethane can be applied to P.V.C. tubing or polyurethane tubing.

'Sextone' is a Registered Trade Mark.

The sieve series for the mesh used herein is the British Standard series.

#### WHAT WE CLAIM IS:—

1. A method a making a catheter or tube

useful for medical or surgical purposes having at the patient end (as herein defined) a coating of a finely-divided, highly X-ray opaque substance, in which to the patient end is applied a paste comprising a finely-divided substance which is high in opacity to X-rays and which has a particle size of not greater than one micron, dispersed in a solution of a synthetic polymer dissolved in at least one organic solvent which is evaporatable and which will soften the synthetic plastics material of which the patient end is made, and allowing the solvent to evaporate to give the coating.

2. A method as claimed in Claim 1 in which the coating is formed by dipping the patient end in the paste.

3. A method as claimed in Claim 1 or Claim 2 in which the synthetic polymer solution is saturated.

4. A method as claimed in any preceding claim in which the weight of highly X-ray opaque substance is about equal to that of the synthetic polymer.

5. A method as claimed in any preceding claim in which the synthetic polymer is polyvinyl chloride or polyurethane.

6. A method as claimed in any preceding claim in which the highly X-ray opaque substance is bismuth, precipitated barium sulphate or tungsten.

7. A method as claimed in any preceding claim in which the solvent is cyclohexanone, methyl ethyl ketone, tetrahydrofuran or mixtures thereof.

8. A method as claimed in any preceding claim in which the paste used is substantially as herein described with reference to either Example.

9. A catheter or tube useful for medical or surgical purposes when made by a method as claimed in any preceding claim.

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